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Agricultural polymers for controlled release of herbicide based on nitrogen-phosphorous polymers

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A novel synthesis of a polymeric herbicide system based on phosphorous-nitrogen containing polymer has been carried out by melt polycondensation of phenyl phosphonic dichloride with N-(2,4-dichlorophenoxyacetyl)diethanolamine **1** (2,4-D diolamide). The polymer is characterized by elemental analysis and IR spectroscopy. The release of 2,4-dichlorophenoxyacetic acid (2,4- D) from the polymer has also been investigated.

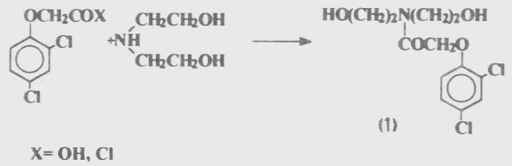
Contamination of ground water by agrochemicals has become a serious issue. Over application and point source contamination increase the pollution potential[1]. Over the last few years, controlled release technologies have emerged as one approach promising to solve the problems which inevitably accompany the use of such agrochemicals[2]. Controlled release formulations are used to maintain effective local concentration agrochemicals in the soil and to reduce the run off. In addition, the number of frequent application required in the growing season can be reduced through the use of controlled release technology[3,4]. As a part of an ongoing project in our laboratory we have produced some reviews concerning this area[3,5] and other publications regarding controlled release pesticide/fertilizer combinations from tartrate or glutarate or polyurea residues and from polyacrylamide gel derivatives[6-8]. We now report a parallel series of controlled release polymers containing nitrogen- phosphorous in addition to herbicidide[2,6,7]. As reported earlier this system might help to minimize the side effects which often accompany the traditional application of pesticides. Also, the polymer carrier in this work which have nitrogen and phosphorous in the backbone when degraded might be useful as a source of nitrogen and phosphorous to the crop growth and to the soil, in contrast to when using inert polymers as carriers that could accumulate in the soil and probably create environmental problems. The synthesis and characterization of polymers containing 2,4-D as a herbicide and phosphorous and nitrogen in their main backbone have been described in the paper. To the best of our knowledge the use of phosphorous-nitrogen containing polymer as a carrier for agrochemical has never been described earlier in the literature.

Results and Discussion

Monomer synthesis: Synthesis of 2,4-D diolamide

2,4-D was selected as the active species because it is known to be a selective herbicide, translocatable with the properties of growth substances, and is used for post-emergence control of annual and perennial broad-leaf weeds in cereals and sugar cane. It is also effective for the protection of many other crops[2]. In addition 2,4-D is commercially available at a price making it suitable for large scale use. It is non-toxic to fish and bees and it's degradation and metabolic pathways are known[9,10]. 2,4-D diolamide has been synthesized by two methods from 2,4-D dichlorophenoxyacetic acid or it's acid chloride and diethanolamine. The reaction is as outlined in Scheme I.

The NH group of diethanolamine can react directly with the COOH group of 2,4-dichlorophenoxyacetic acid (2,4-D) to liberate H_2O as a byproduct at high temperature (135-140°C) [method(a)]. It can also react at low temperature with the acid chloride of 2,4-D using pyridine as an acid acceptor [method(b)]. Both procedures were used to synthesis 2,4-D diolamide monomer.



Scheme I – Synthesis of 2,4-D diolamide monomer.

In procedure (a) the reaction was carried out in melt without solvent at temperature 135-140°C; the yield of this procedure was relatively low (40%).

In procedure (b), which was described by our laboratory[11], 2,4-D diolamide was synthesized from the acid chloride of 2,4-D and diethanolamine in benzene using pyridine as an acid acceptor. The reaction takes place almost at low temperature. The yield in this procedure was found to be higher.

The product obtained in both methods was examined by thin layer chromatography (TLC) using a mixture of diethyl ether-dioxane (6.5:3.5) as eluent which showed one component indicating the product to be relatively pure. The structure of this monomer (1) was established by elemental analysis and IR and ^{1}H NMR spectral data. The elemental analysis for 2,4-D diolamide monomer agreed well with the chemical structure **1** shown in Scheme I. The IR spectrum showed an absorption band at 1067 cm^{-1} for the ether linkage of other expected absorption bands. The ^{1}H NMR spectrum of 2,4-D diolamide monomer supported the assumed structure. Three aromatic protons appeared at δ 6.97 ppm, hydroxyl protons at 4.71 ppm and OCHO and NCHC protons at 5.07and 3.3-3.58 ppm respectively.

Polymer synthesis and characterization Polyphosphonate containing 2,4-D **2** was synthesized by polymerization of phenylphosphonic dichloride with 2,4-D diolamide as shown in Scheme II. The polymer was synthesized by melt polycondensation method without any solvent or catalyst. Evolution of hydrochloric acid gas was observed at 30°C and detected with ammonia paper. The polymerization was continued further for 4 hr under vacuum to remove any by-product (HCl) and to eliminate depolymerization reaction. The inherent viscosity which was measured in DMF solution (0.5 g/dL at 30°C) was 0.16; the yield of polymer was 80%. The resulting polymer is soluble in methanol, acetone, dichloromethane and insoluble in ether, petroleum ether and dodecane.

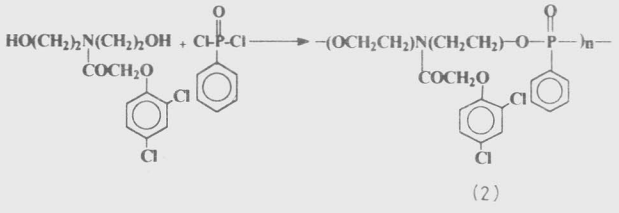
It is almost soluble in polar organic solvents. This might be due to the presence of phosphorus and flexible non symmetrical P-O-C linkage in the main-chain, because incorporation of phosphorous in a compound increases its polarity and solubility[12,13].

The chemical structure of the polymer **2** was determined on the basis of the elemental analysis and IR spectrum. The results are in agreement with the assigned structure shown in Scheme II. However no polymer was obtained when the polymerization were carried out at room temperature in chloroform using triethyl amine as an acid acceptor.

Release studies Release of 2,4-D from the polymer was evaluated under different conditions of buffer solutions or different temperatures. It is found that the release rate in buffer solution of *p*H 4 is slower than in pH 7 or *p*H 9.2 (cf. Figure 1). Also, the release rate is increased by increasing the temperature from 25°C to 50°C (cf. Figure 2). This may be due to the acceleration of hydrolysis of 2,4-D herbicide from the polymer with the increase in temperature.

Experimental Section

Reagents. 2,4-Dichlorophenoxyacetic acid (2,4-D) was supplied from Aldrich and was recrystallized twice from benzene (m.p. 142- 44°C). Diethano-



(2)

Scheme II – Polycondensation of 2,4-D diolamide with phenyl phoshonic dichloride.

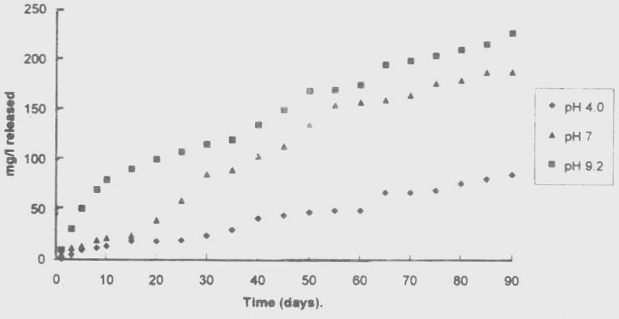


Figure 1—Release profiles of 2,4-D from polymer **2** at different *p*H values.

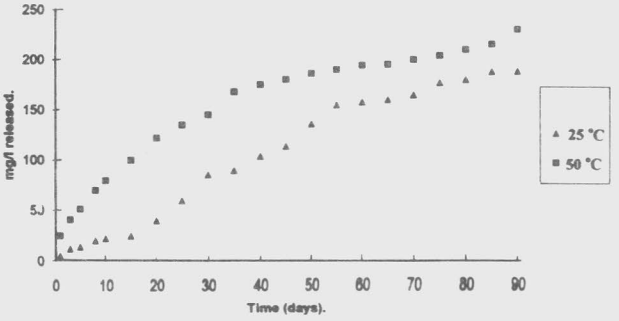


Figure 2—Release profiles of 2,4-D from polymer **2** at different temperatures.

lamine was supplied from Aldrich and was purified by distillation under reduced pressure. Phenylphosphonic dichloride (Aldrich) was purified by vacuum distillation prior to use; b.p. 130-131°C/13 torr (lit. b.p.143°/25 torr). 2,4-D acid chloride (2,4-DC) was synthesized as described by us earlier[2]. The procedure is as follows:

To 2,4-D (26.5 g, 120 mmoles) was added thionyl chloride (14.6 mL, 23.8 g, 200 mmoles). The mixture was refluxed at 100°C under dry conditions for 5 hr. The excess thionyl chloride was distilled off and dry toluene added to it. The last traces of thionyl chloride were co-distilled off with toluene using a rotary evaporator. The product was dried in vacuum at room temperature overnight. Essentially 100% of viscous oil was achieved.

Characterization. Viscosity measurements were carried out with 0.5 % (w/v) polymer solutions in DMF at 30°C using Ubbelohde suspended level viscometer. The elements, viz. carbon, hydrogen, nitrogen, halogen, and phosphorous were analyzed on a Carlo Erba instrument. IR were recorded in KBr pellets on a Nicolet 20 SXB spectrometer. ^{1}H NMR spectra were recorded on a Bruker WM 250 (250 MHz) spectrometer using $CDCl_3$ as solvent, and tetramethylsilane as internal standard. This layer chromatography (TLC) for monomer was carried out on 0.25 mm silica gel pre-coated plates containing a fluorescent indicator (Aldrich).

Synthesis of 2,4-D diolamide monomer (Scheme I). 2,4-D diolamide was synthesized by the following two methods.

Procedure (a). To 2,4-D (22.1 g, 100 mmoles) placed in a two necked flask diethanolamine (21.02 g, 200 mmoles) was added under nitrogen atmosphere and dry conditions. The reaction mixture was stirred and heated in an oil-bath gradually to 135- 140°C. The heating was continued for 6 hr and the reaction mixture cooled to room temperature and poured into stirred water. The stirring was continued for about 3 hr when a white solid product precipitated out. It was filtered on a sintered glass G3 funnel. The product was recrystallized from benzene and dried under vacuum at 50°C overnight, m.p. 92-95.3°, yield 40%.

Procedure (b)

To a solution of diethanolamine (26.2 g, 274.6 mmoles) in dry benzene in a two-necked flask, dry pyridine (10 mL, 124 mmoles) was added under dry conditions. The reaction mixture was ice cooled to −5°C using ice-salt mixture, and then a solution of 2,4-D acid chloride (2,4-DC) (100 mmoles, 23.95 g) in benzene added to it dropwise while stirring. After the addition of 2,4-DC was over, the reaction mixture was stirred under ice cooling for 5 hr, and stirring continued at room temperature for another 24 hr. The product was filtered, washed with deionized water and ether, and recrystalized from dichloromethan; yield 22.5 g (73.0%). The product was characterized by elemental analysis and IR and ^{1}H NMR spectral data (Found: C, 49.0; H, 5.5; N, 4.2; Cl, 21.2.$C_{12}H_{15}NO_4Cl_2$ requires C, 46.7; H, 4.9; N, 4.5; Cl, 23.0%.IR spectrum showed absorption bands at 1076 (ether linkage), 3100 (CH aromatic), 2860 (CH aliphatic), 1652 (C=O), 1486 (C=C aromatic), 866 and 804 (CH aromatic), 865, 822 (C-Cl stretching) and 3400 cm^{-1}(OH). ^{1}H NMR spectrum exhibited peaks at δ 6.97 (3H, m, aromatic), 5.07 (2H, s, C-CH_2O), 4.71 (2H, s, OH) and 3.31-3.58 (8 H, m, 2xN-CH_2CH_2).

Polymerization of 2,4-D diolamide with phenylphosphonic dichloride using melt polymerization technique (Scheme II) To 2,4-D diolamide (4g, 12.3 mmoles) was added phenylphosphonic dichloride (1.575 mL, 12.3 mmoles) and the reaction mixture heated under dry conditions gradually to 90°C under nitrogen atmosphere. The heating was continued at 90°C for 4 hr and then the temperature raised gradually to 170°C for another 4 hr. The reaction was continued further under vacuum for 2 hr. After polymerization was complete the product was washed with pet. ether to remove the unreacted phenylphosphonic dichloride and dried under vacuum at 50°C, yield 80%. Found (Calcd)(%): C, 47.1 (50.0); H, 4.2(4.1); N, 2.8(3.0); Cl, 17.0(16.5); P, 6.0(7.0); IR spectrum showed complete disappearance of hydroxyl groups of 2,4-D diolamide, and the appearance of bands at 3100-3000 (CH aromatic), 3000-2800 (CH aliphatic), 1735(C=O), 1585, 1472 (C=C aromatic), 1086 (COC), 801 (CH aromatic) and 800-600 cm^{-1} (C-Cl).

Release rate measurements. Release of 2,4-D from the polymer system was measured by placing 100 mg of the herbicide in 100 mL buffer solution at different *p*H (4,7,9.2) values at 25°C. The release of 2,4-D was monitored by removing a sample from the buffer medium from time to time and analyzing it on a UV spectrophotometer at 283 nm. The profiles of the

amount released from the polymer system are shown in Figure 1. The experiment was repeated with buffer solution of *p*H 7 at 50°C to study the effect of temperature on the release rate. The release profiles of 2,4-D at two different temperatures are shown in Figure 2.

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